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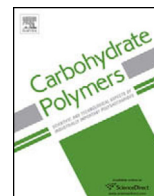
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Water absorption, retention and the swelling characteristics of cassava starch grafted with polyacrylic acid



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ABSTRACT

An important application of starch grafted with copolymers from unsaturated organic acids is the use as water absorbent. Although much research has been published in recent years, the kinetics of water absorption and the swelling behavior of starch based superabsorbents are relatively unexplored. Also, water retention under mechanical strain is usually not reported. Cassava starch was used since it has considerable economic potential in Asia. The gelatinized starch was grafted with acrylic acid and Fenton's initiator and crosslinked with N,N'-methylenebisacrylamide (MBAM). Besides a good initial absorption capacity, the product could retain up to 63 g H₂O/g under severe suction. The material thus combines a good absorption capacity with sufficient gel strength. The mathematical analysis of the absorption kinetics shows that at conditions of practical interest, the rate of water penetration into the gel is determined by polymer chain relaxations and not by osmotic driven diffusion.

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1. Introduction

1.1. General

Superabsorbent polymers (SAP) are materials which can absorb and retain a large amount of water or aqueous solutions. According to the Global Industry Analysts, Inc. report, it is projected that the world demand for superabsorbent polymers will reach up to 1.9 million metric tons in 2015. The fast increase in demand will be seen in the developing markets and in new applications (N.A., 2010). Superabsorbents were first developed in the US Dept. of Agriculture by grafting acrylonitrile (AN) onto corn starch and saponifying the product. Although at present superabsorbents consisting of fully synthetic polyacrylic acid dominate the market because they are cheaper to produce, research on starch-based superabsorbents is of growing interest again (Jyothi, 2010; Zohuriaan-Mehr & Kabiri, 2008). Waste disposal concern, increasing prices of petrochemical feed stocks as well as the desire to use renewable resources are driving this interest. To become more competitive, high water absorbency and higher gel strength are of great importance. The

main incentive for our research project however was to find new applications of cassava starch. This is a renewable source of raw material which is abundantly available and relatively cheap in Asia, more specifically in Indonesia. Currently, the economic potential of cassava is not fully exploited which would make the development of possible industrial applications of particular interest (Witono, Noordergraaf, Heeres, & Janssen, 2012).

Superabsorbent materials consist of crosslinked hydrophilic polymer chains forming a 3-dimensional network structure. Both starch and vinyl monomers like acrylic acid, acrylamide, acrylonitrile and polyvinyl alcohol (PVA) are of interest as they contain a number of hydrophilic functionalities in their structure like hydroxyl and carboxyl groups. Ample literature reports and both older and recent patents (Chambers, 2010; Masuda, Nishida, & Nakamura, 1978) can be found on superabsorbent production based on starches, e.g. from wheat, corn or potato (Athawale & Lele, 2000; Athawale & Lele, 2001; Hashem, Afifi, El-Alfy, & Hebeish, 2005; Masuda et al., 1978; Qunyi & Ganwei, 2005; Weaver et al., 1977; Wu, Wei, Lin, & Lin, 2003). The use of cassava starch for this application is relatively novel since only few reports have appeared so far (Lanthong, Nuisin, & Kiatkamjornwong, 2006; Parvathy & Jyothi, 2012; Sangsirimongkolying, Damronglerd, & Kiatkamjornwong, 1999). Also, many papers deal with the indirect synthesis involving the grafting of starch with acrylonitrile or acrylamide followed by a hydrolysis reaction. Direct grafting of acrylic acid onto starch would eliminate the necessity of this second

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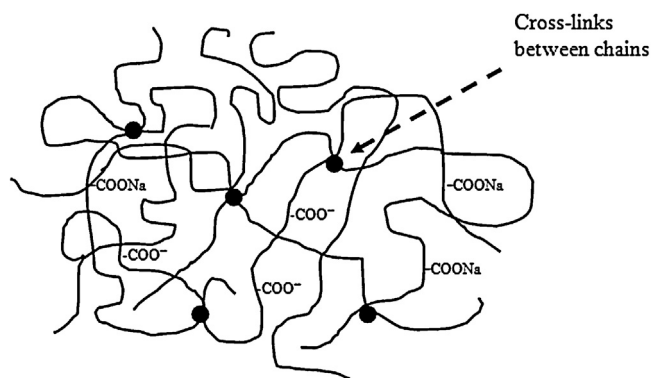


Fig. 1. Schematic view of a cross-linked polymer network (Buchholz & Graham, 1998).

process step, thus simplifying the synthetic route considerably. The process of Sanyo Chemical Industries as patented by Masuda et al. (1978) was based on this route but has not been a commercial success probably for economic reasons of the time.

In the present study, direct grafting of acrylic acid onto gelatinized cassava starch was performed in the presence of a crosslinker (N,N'-methylenebisacrylamide) using Fenton's initiation system ($\text{Fe}^{2+}/\text{H}_2\text{O}_2$). This initiator has the advantage of being cheap, non-toxic and of operating at mild conditions (40°C , atmospheric pressure). Also, the system is probably easier to scale up than irradiation initiation methods like those used by H  rold, Fouassier, and Cedex (1981) and Kiatkamjornwong, Mongkolsawat, and Sonsuk (2002). Because of the non-selective initiation, formation of acrylic acid homopolymer is inevitable. It is likely however that the polymerization crosslinker will incorporate a certain part of this homopolymer into the grafted network. The hydrogel product was analyzed to determine the efficiency of the grafting reaction. Furthermore, product properties like the capacity to absorb and retain water at different ratios of starch to monomer, various levels of crosslinking and at various degrees of neutralization were determined. A large capacity to absorb water is reported in many papers, but measuring the potential of starch based materials to retain the absorbed water under conditions that exert mechanical force on the material is a novel aspect of this work. Also, no inorganic fillers like clays were used. The method to assess the retention potential under force was newly developed.

An unexplored aspect of starch based superabsorbents is the kinetics of water absorption. The mathematical analysis of the absorption behavior results in valuable insight into the factors that determine the rate of water penetration into the gel.

1.2. Mechanisms of swelling in hydrogel copolymer

Grafting acrylic acid onto starch in the presence of a polymerization crosslinker leads to the formation of a polymer network that is loaded with negative charged COO^- groups, as shown schematically in Fig. 1. Due to electrostatic repelling interactions, the chains stretch out thereby providing spaces inside the polymer networks which can absorb and retain a large volume of water or aqueous solutions, e.g. human body fluids. Moreover, the hydroxyl groups from starch and carboxyl groups from acrylic acid are hydrophilic and have a high affinity for water. The crosslinking of the polymer chains, e.g. with N,N'-methylenebisacrylamide is essential to the formation of a network in order to make the copolymer insoluble in the aqueous environment. It does restrict the expansion capability of these networks but increases the mechanical strength of the gel, which are conflicting demands in fact. From literature it is

known (Buchholz & Graham, 1998) that the level of crosslinking must thus be optimized against these demands.

Neutralization by adding sodium hydroxide replaces H^+ ions of carboxylic groups by Na^+ . Upon contact with water these sodium ions are hydrated which reduces their attraction to the carboxylate ions. This allows the sodium ions to move more freely inside the network, which contributes to the osmotic driving force for the diffusion of the water into the gel. As such, neutralization increases the water absorption capacity.

1.3. Kinetic analysis of water sorption: theory and literature overview

In relation with the intended application of the product as a superabsorbent, swelling kinetics is an important part of this work. When a copolymer gel is immersed in water, the water diffuses into the polymer matrix and the material starts swelling. The migration of water into dynamically formed spaces between macromolecule chains continues until it reaches the equilibrium state. Extensive reviews have been published on the mechanism of water diffusion into swellable polymers. Generally, the mathematics that governs the mass transport phenomena by diffusion is based on Fick's second law. The basic form is given by Eq. (1):

$$\frac{\partial C(x, t)}{\partial t} = D \frac{\partial^2 C(x, t)}{\partial x^2} \quad (1)$$

where C is the concentration, x the distance parameter, t the time and D is the diffusion coefficient of water into the polymer matrix.

For diffusion into a cylinder and sphere, the parameter x in Eq. (1) is replaced by the radial distance:

$$\frac{\partial C}{\partial t} = \frac{1}{r} \frac{\partial}{\partial r} \left(r D \frac{\partial C}{\partial r} \right) \quad (2)$$

where r is the radius of cylinder or sphere.

Crank (1975) derived analytical solutions for many materials, shapes and conditions, based on Fick's law. However, he indicated that this model cannot describe the system satisfactory when diffusing molecules cause an extensive swelling of the material in which case the ability of the network to swell may become the limiting factor. That situation is characteristic for many industrial polymer superabsorbents and foodstuff applications but has not really been explored yet for starch based absorbents.

An extension of the Fick's law to compensate for this swelling, was proposed by Crank (Crank, 1975) and followed by other authors (Alfrey, Gurnee, & Lloyd, 1966; Camera-Roda & Sarti, 1990; De Kee, Liu & Hinestroza, 2005; Franson & Peppas, 1983; Frisch, 1980; Fuhrmann, 1979; Puri, Liu, & De Kee, 2008; Rogers, 1985). The mass transport in macromolecular material involves a complex process, which can be influenced among others by the internal structure of the polymer (De Kee et al., 2005; Franson & Peppas, 1983), glass transition temperature (Wikipedia, 2011), effects of swelling and relaxation and the retardation time of the polymer matrix (Puri et al., 2008), the chemical nature of the diffusing molecules (Rogers, 1985) and mechanical deformation (De Kee et al., 2005).

The diffusion behavior of water into polymers networks can be divided into three basic classes, based on the relative rates of diffusion and polymer relaxation. Case I: Fickian diffusion in which the rate of transport is much lower than the relaxation of the polymer chains. Case II: diffusion is very rapid compared with the relaxation process. Then the rate of water movement is determined by this relaxation, or the restrictions imposed by the network swelling capability. There is also an intermediate case: non-Fickian or anomalous diffusion, which occurs when the diffusion and relaxation rates are comparable. To cope with these situations, a more general model has been proposed (Bajpai & Johnson, 2005; Frisch, 1980;   z  m, Kundakci, & Karada  , 2006) which is in fact a severe

simplification of Eq. (2), in the form of an empirical power law equation:

$$\frac{M_t}{M_\infty} = kt^n \quad (3)$$

where M_t is the mass of water absorbed at time t , M_∞ is the mass of water absorbed at equilibrium, k is a characteristic constant of the polymer and n is a diffusional exponent. This exponent is in fact the key to this equation since the value of n is dependent on the transport mechanism. For a value of $n < 0.5$, the rate of solute moving into or releasing from the polymer is dominated by a Fickian diffusion mechanism while at higher values the dynamic swelling of the polymer, the macromolecular chain relaxations, is the prevailing factor. At $n=0$ the mass transfer is independent of time, regardless of the geometry. The work of Ritger and Peppas (1987) has demonstrated however that the transition from Fickian to non-Fickian diffusion is at a lower value than 0.5 and is also dependent on the geometry of the absorbing material. Their experiments and calculations show that for a cylindrically shaped gel, the value must be 0.45, with a confidence of 95%. For other geometries like a thin film or a sphere it is even slightly lower, $n = 0.43 \pm 0.01$. We used this more recent work for the analysis of our experiments on sorption kinetics. We do not have accurate knowledge on the shape of our gels but, a purely cylindrical form would be unlikely. Thus, when n is below ca 0.43 we will conclude that Fickian diffusion is the governing factor while at n -values beyond that, we conclude on a non-Fickian mechanism of transport in which the relaxation of the macromolecular chains of the hydrogel determines the rate of water sorption.

2. Experimental

2.1. Materials

The starch used in this experiment was native cassava starch of 99.93% purity, produced by PT. Sungai Budi, Lampung and kindly supplied by PT. AVEBE Indonesia, Cikampek, Indonesia. Acrylic acid glacial P (99.5%) stabilized with 200 ± 20 ppm MEHQ was kindly supplied by BASF PETRONAS Chemicals, Sdn. Bhd., Malaysia and was used without further purification. FAS (ferrous ammonium sulfate), H_2O_2 (hydrogen peroxide) 30% and sodium hydroxide were reagent grade chemicals and were used as received. Analytical grade acetone was supplied by Lab-scan, Analytical Sciences, Ireland. N,N'-methylenebisacrylamide was purchased from Sigma Aldrich (Germany) and used as received.

2.2. Preparation and characterization of the neutralized graft copolymers

Grafted cassava starch was prepared by reacting 7.5% gelatinized starch solution with acrylic acid monomer in the presence of the crosslinker MBAM in a laboratory scale (500 ml) stirred reactor. Full details of the reactor and the equipment were reported in Witono et al. (2012). For the purpose of comparison, graft copolymer without crosslinker was also synthesized. The ratio of dry starch with respect to the acrylic acid monomer was usually 1:2 (mol/mol), but for the optimization of this parameter in some preparations different ratios were applied. Various quantities of MBAM were used: 1%, 1.5%, 2% and 2.5% (% wt. of crosslinker with respect to the total weight of the acrylic acid monomer). The copolymerization reaction was initiated using Fenton reagent (Fe^{2+}/H_2O_2). The initiator concentration was 0.01 mol Fe^{2+} /kg of total reaction mixture and H_2O_2 to Fe^{2+} molar ratio was 10:1. We found that the addition of MBAM to the aqueous solution resulted in an inhomogeneous product, probably due to the poor water solubility of the crosslinker. This is an unexpected finding as it was not reported in other

publications. The problem could be solved by first mixing MBAM with the acrylic acid before addition to the reaction solution. The reaction was run for 2 h at 40 °C. Samples from the reaction product were analyzed for the grafting parameters using a method of analysis involving complete homopolymer separation and quantitative analysis by HPLC and 1H NMR. The method was especially developed for this project and has been reported in full detail before (Witono, Marsman, Noordergraaf, Heeres, & Janssen, 2013). However, the complete separation of crosslinked homopolymer from the product is more difficult than in the system without crosslinker. Some of the homopolymer may have become intensively entangled into the grafted chains, especially when it gets strongly crosslinked in itself as well. It stays in the precipitate and is measured in the values of the add-on and the graft selectivity (GE). This would not be a disadvantage for the product as such when this homopolymer does not drift out of the gel upon application.

A portion of 20 g, a representative sample of the original reaction product, was neutralized by the addition of sodium hydroxide. The NaOH was added in different mole ratios to the monomer (from 0.25, 0.50, 0.75 to 1.00, the stoichiometric equivalent ratio), dissolved in 2 ml distilled water. The color changed from reddish-brown to pale yellow in about 10 min. After neutralization, excess acetone was added to precipitate the grafted product and to separate it from the homopolymer and possible monomer residues. The precipitate was washed with distilled water to remove initiator salts and the pH was maintained at 7, if necessary, by addition of a small amount of dilute hydrochloric acid. Finally, the precipitate was dried in the oven at 50 °C for 24 h till constant weight and stored in a sealed container.

2.3. Water absorption capacity (WAC) measurement

To determine the water absorption capacity of the products, a gravimetric method was applied. An accurately weighed quantity of the sample (0.25 g) (m_1) was immersed in 100 ml of distilled water at room temperature, and allowed to reach the maximal swelling. For practical purposes we use M_{max} as an end value for further calculations. For the determination of sorption kinetics, tests were run where at intervals of 30 min the swollen sample was separated by filtration through a 100 mesh-sieve aluminum screen. It was then weighed (m_2). The water absorption capacity (WAC) is calculated as g H_2O /g dry copolymer using the following equation:

$$WAC \text{ (g/g)} = \frac{m_2 - m_1}{m_1} \quad (4)$$

where m_2 means the weight of sample with the absorbed water, whereas m_1 is the initial weight of the dried sample. In all cases, measurements were conducted till and just beyond the maximum absorption capacity so the end times will be different for the various samples.

2.4. Water absorption capacity measurement under near-vacuum suction

In this experiment, the water absorption capacity of the product under suction was measured using vacuum filtration. Similar to the water absorption capacity measurement, an accurately weighed quantity of the dry sample (0.25 g) (m_1) was soaked in 100 ml of distilled water at room temperature and allowed to reach its maximal swelling. In order to determine whether the maximum absorption capacity was reached, the weight of the sample was measured every 30 min. At intervals of 30 min the swollen sample was separated from the solution. In these tests, a Büchner funnel was used applying vacuum suction (equivalent to a pressure of 22.1 kPa). Then, the swollen sample was weighed (m_2). The water absorbency capacity was also calculated using Eq. (4), but in this case, the resulting

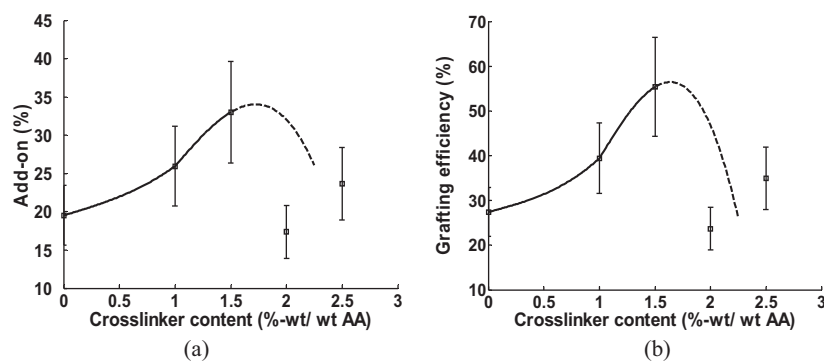


Fig. 2. Add-on (a) and GE (b) as a function of the ratio of MBAM to acrylic acid. The bars represent the deviation between various experiments, the points are the average of at least two runs [Reaction conditions: 7.5% cassava starch in water, starch to monomer 1:2 (molar ratio), FAS 0.01 mol/l, $\text{H}_2\text{O}_2/\text{Fe}^{2+}$ ratio 2:1, 40 °C, reaction time 120 min].

value is the amount of water retained in the material under severe suction.

3. Results and discussion

3.1. Characterization of the product

To characterize the extent and efficiency of the grafting reaction, parameters like add-on and grafting efficiency (GE) are commonly used (Athawale & Rath, 1999; Park, Song, & Song, 1999; Patil & Fanta, 1993; Vera-Pacheco, Vázquez-Torres, & Canché-Escamilla, 1993). Add-on depicts the weight ratio of the grafted polymer to the total grafted product. The grafting efficiency represents the selectivity of the grafting reaction, being defined as the ratio of grafted versus total polymer produced.

The effect of the crosslinker to monomer ratio (CL%) on the grafting parameters is shown in Fig. 2a and b. The experimental trend for both of the graft result parameters is the same: first a firm increase in the graft results followed by a decrease after ca 1.5% crosslinker dosage. The reason for this optimum is not clear yet. However, the initial trend toward higher values of GE when crosslinker is applied is clear. There are two possible explanations for this observation. A part of the heavily crosslinked homopolymer may become so strongly entangled with the grafted chains that it cannot be separated by the analytical method, as reported already in Section 2.2. A second possibility is that one double bond of the crosslinker, which is also activated by the non-selective initiator radicals, reacts with a growing graft while the other can get reacted into a chain that would have become homopolymer. Then, a chemical connection is formed that increases both add-on and GE. It cannot be measured what the exact contribution of each of these effects will be, but it is probable that they both occur. Perhaps we should regard the measured values therefore as 'apparent' add-on/GE.

It must be mentioned that such results, especially the course of GE versus crosslinker dosage, are only scarcely reported in literature. In many recent papers, the grafting result parameters are just bypassed and instead a direct relation between the reaction variables and the absorption capacity is made. Although this direct approach is certainly of value, we believe that the additional information on the graft result parameters will ultimately contribute to a better understanding of the interaction between the material composition and its properties. The few data that were found on the course of GE versus CL% (e.g. Lanthong et al., 2006) show a comparable optimum. In our work, the value of GE at the peak is ca 55%, which means that there is still free homopolymer as well. The optimum add-on achieved is close to 33%.

At more than 2% crosslinker content, the graft parameter values tend to go down. It is well known (ScienceLab.com, 2008) that

crosslinker molecules may also get involved in an autopolymerization reaction making it unable to perform the intended crosslinking action, especially when there is an oxidizing agent in the system. It is questionable whether this may also occur at just 2–2.5 CL% already. Just another possible explanation for the observed results is that at increasing density of the gel, the polymerization reaction may get retarded because of mass transfer limitations. The results are indisputable but such possible explanations must be further studied.

3.2. Behavior of gels at varying degree of neutralization (DN) and crosslinker levels

3.2.1. Effect of the degree of neutralization (DN)

The effect of the degree of neutralization of the starch grafted acrylic acid by NaOH was investigated. For both mole ratios of starch to acrylic acid (1 and 0.5) and over the whole range of concentrations of crosslinker addition (1–2.5%), it was found that the highest absorption capacity was always obtained at ca 50% neutralization. This can be concluded from the data shown in Figs. 3 and 4. Since DN was defined as a percentage of the monomer added, the amount of water attracting PAA- Na^+ groups is higher at the lower ratio of starch to monomer. In that system with constant amount of starch, there is more monomer present and therefore more grafted PAA will be formed. This explains why WAC is higher at the lower starch to monomer ratio at the same relative level of neutralization.

Other authors tend to find the optimum WAC at higher degrees of neutralization, e.g. Kanbayashi and Kato (1994) and Li, Zhang, and Wang (2005) in the range up to 85%. Zhang, Wang, Gu, and Zhang (2007) found the maximal WAC from polyacrylate/bentonite superabsorbent at DN in the range 50–75%. Such differences may be due to other levels of crosslinking and other structural properties or whether the DN is defined on basis of the monomer like in this work or with respect to truly grafted carboxylic groups.

As mentioned before, neutralization increases the amount of Na^+ ions attached along the macromolecular chains. This should increase the osmotic driving force for water absorption so that higher levels of WAC must be expected. In this work we found that grafted copolymer has the best WAC at ca 50% DN. When more NaOH is added (75% DN or 100% DN), the ability of the copolymer to absorb water is worse. It seems that part of the gel dissolves again. This may be because only up to 50% of the monomer has really been taken up in the grafted polymer network, as shown in Fig. 2. It means that Na^+ ions present in amounts exceeding this figure do not interact with carboxylic groups and as such do not contribute to enhanced ionic-osmotic pressure. Perhaps some starch chains may even be broken down by the effect of excess basic ions. Surprisingly,

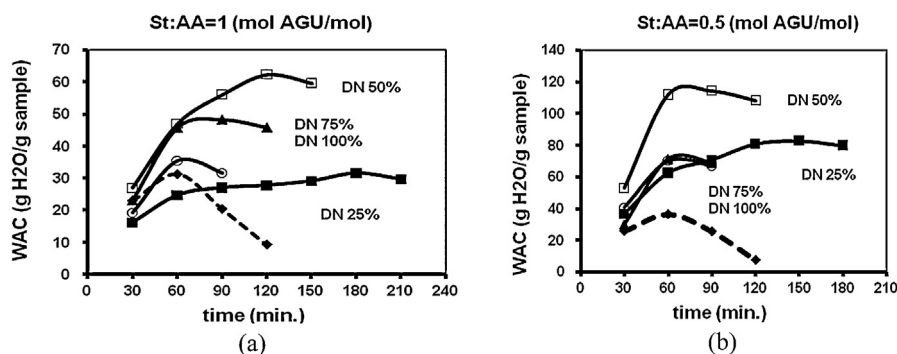


Fig. 3. Water absorption capacity (WAC) of the grafted copolymer with 2% crosslinker addition, at different mole ratio starch to AA = 1 (a) and 0.5 (b) (--- without neutralization and crosslinker addition).

water absorbency up to half of the maximum WAC was already found with several samples before neutralization and without the crosslinker added, but the absorption capacity is clearly not stable over time. This just confirms the necessity of using the crosslinker, to form and hold together a stable network.

3.2.2. Effect of time

From Fig. 3a and b it can be seen that after the maximum water absorbency has been achieved, the WAC of copolymers is gradually reduced over time. The graphs show that this effect is more pronounced at a lower level of crosslinking. As stated in Section 2.2, some strongly entangled homopolymer will probably still be in the product. When the material is exposed to excessive amounts of water, some of that may still get disentangled and then slowly drifts out of the gel. This is the most likely explanation for the occurrence of a maximum in the WAC versus time. This effect is most pronounced at the lowest crosslinker addition, and very clear at zero crosslinker in the system. This observation fits to the idea that some of the otherwise free homopolymer gets connected into the network by the crosslinking reaction. It certainly shows that the gel strength, the coherence of the material, has an important role in determining the amount of water that can be absorbed and retained inside the hydrogel.

3.2.3. Effect of the amount of crosslinker added

Fig. 4 shows both the effect of the crosslinker (MBAM) to acrylic acid ratio as well as different degrees of neutralization, on the maximum water absorption capacity of the copolymer. It can be seen that the variation of the amount of crosslinker has a larger impact on the water absorption capacity of the grafted product than the degree of neutralization. The graph shows a maximum in WAC, a trend which is also observed in fully synthetic superabsorbent materials, e.g. Buchholz and Graham (1998). MBAM brings about crosslinking between two or more macromolecules by forming covalent bonds. In this way a network is formed that prevents dissolution of the structure while on the other hand a porous network is formed in which water can be entrapped. Up to the 2% cross-linker added, the water absorption capacity increases up to 114 g H₂O/g dry sample (for 50% DN), but above that percentage WAC drops rapidly, to 69 g H₂O/g at 2.5% CL. At higher degree of

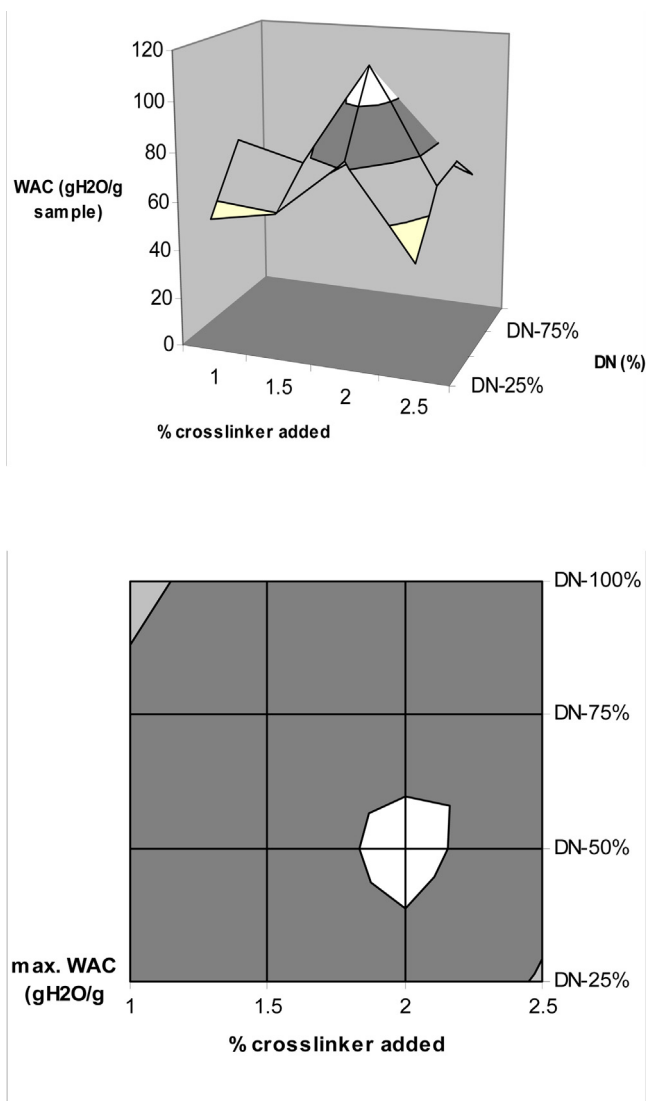


Fig. 4. Water absorbency as a function of the amount of crosslinker added and the degree of neutralization (DN). Cassava starch grafted with AA at a ratio of starch to monomer of 0.5. The second figure is a top-down view of the 3D plot. The white area represents the optimal WAC.

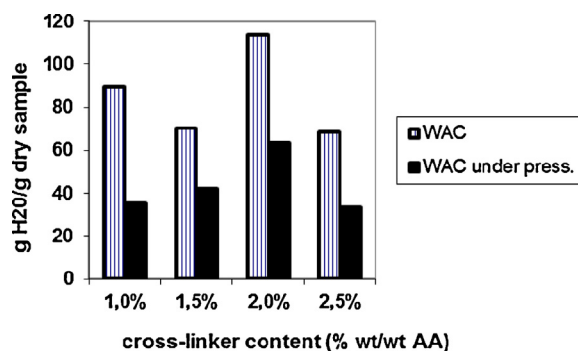


Fig. 5. Water absorption capacity of the PAA-grafted starch with and without applying external suction.

Table 1
Calculated diffusional exponents for water absorption kinetics, from Eq. (3) and for various samples.

		<i>k</i>	<i>n</i>	<i>R</i> ²	Transport mechanism
St:AA = 2:1	DN 25%	0.3865	0.2055	0.9831	Fickian
	DN 50%	0.0963	0.4527	0.9978	Non-Fickian
	DN 75%	0.1147	0.4361	0.9387	Non-Fickian
	DN 100%	0.0659	0.6107	0.9877	Non-Fickian
St:AA = 2:2	DN 25%	0.0769	0.5785	0.9688	Non-Fickian
	DN 50%	0.1009	0.4691	0.9706	Non-Fickian
	DN 75%	0.41	0.7193	0.9719	Non-Fickian
	DN 100%	0.0685	0.5793	0.8911	Non-Fickian
+CL 1%	DN 25%	0.1226	0.4019	0.977	Fickian
	DN 50%	0.0634	0.5597	0.9783	Non-Fickian
	DN 75%	0.085	0.5571	0.9555	Non-Fickian
	DN 100%	0.0173	0.9043	0.9969	Non-Fickian
+CL 1.5%	DN 25%	0.1903	0.3526	0.9776	Fickian
	DN 50%	0.1343	0.4184	0.9644	Intermediate
	DN 75%	0.0892	0.5535	1	Non-Fickian
	DN 100%	0.0286	0.7956	0.9979	Non-Fickian
+CL 2.5%	DN 25%	0.2029	0.3087	0.9508	Fickian
	DN 50%	0.0733	0.5521	0.995	Non-Fickian
	DN 75%	0.071	0.6004	0.9224	Non-Fickian
	DN 100%	0.1775	0.4055	1	Fickian
St:AA = 2:3	DN 25%	0.1675	0.2638	0.9585	Fickian
	DN 50%	0.0319	0.7261	0.9528	Non-Fickian
	DN 75%	0.0375	0.7403	0.968	Non-Fickian
	DN 100%	0.1401	0.4233	0.9087	Non-Fickian
St:AA = 2:4	DN 25%	0.3837	0.1233	0.8253	Fickian
	DN 50%	0.0617	0.5715	0.958	Non-Fickian
	DN 75%	0.0224	0.8589	0.9413	Non-Fickian
	DN 100%	0.0125	0.9803	0.9983	Non-Fickian
+CL 1%	DN 25%	0.1009	0.4542	0.968	Non-Fickian
	DN 50%	0.0503	0.6788	1	Non-Fickian
	DN 75%	0.0282	0.8126	0.8802	Non-Fickian
	DN 100%	0.0229	0.8584	0.8933	Non-Fickian
+CL 1.5%	DN 25%	0.1365	0.3882	0.9303	Fickian
	DN 50%	0.0303	0.7867	0.9	Non-Fickian
	DN 75%	0.0195	0.8894	0.9489	Non-Fickian
	DN 100%	0.0385	0.74	0.90	Non-Fickian
+CL 2%	DN 25%	0.1101	0.4499	0.9802	Non-Fickian
	DN 50%	0.0674	0.6148	0.8886	Non-Fickian
	DN 75%	0.0626	0.6355	1	Non-Fickian
	DN 100%	0.1629	0.4194	1	Intermediate
+CL 2.5%	DN 25%	0.1597	0.3444	0.9368	Fickian
	DN 50%	0.0685	0.5733	0.9612	Non-Fickian
	DN 75%	0.0321	0.7389	0.9366	Non-Fickian
	DN 100%	0.0439	0.6695	0.9361	Non-Fickian

crosslinking, the average distance between two crosslink or knotting points will become shorter. This will greatly affect the ability of the polymer chains to move in order to create space for the water, and of the material as a whole to swell. Then the macromolecules tend to become a stiff structure instead of the flexible network. This observation conform to well established theory (Flory, 1953) and also to the results from Omidian, Hashemi, Sammes, and Meldrum (1998). There is not a theory yet, however, that allows for quantitative predictions for a specific material thus water absorbency must be measured for each new material. The conditions that give the optimal WAC for our material are illustrated in the form of a 3D plot and a top-down view of that, in Fig. 4.

It is remarkable that there seems to be no direct or simple relation between the grafting parameters and absorption capacity. The best grafting result was obtained at 1.5% crosslinker addition which does not correspond to the highest absorbency. Comparable observations were made however by Kiatkamjornwong et al. (2002)

and by Lanthong et al. (2006). Clearly, this subject should be further investigated. When a reason for this behavior is found, it will give a better understanding of the interaction between molecular and bulk material properties. Such would facilitate further development of the superabsorbent product. The optimum amount of crosslinker added (2%) that gives the highest WAC is the same value as found for a hydrogel based on the graft copolymer of cassava starch with acrylamide and itaconic acid by Lanthong et al. (2006).

The maximum water absorbency of 114 g H₂O/g sample is good but still a little below the values seen in literature for comparable biobased hydrogels. Results from starch-based hydrogels show a wide range of maximal absorption capacities, but they are usually lower than for fully synthetic materials. For example, acrylic acid-grafted starch using ceric ammonium nitrate initiator as made by Masuda et al. (1978) and Athawale and Lele (1998) shows WAC values of ca 200 g/g. But initiation by irradiation with γ -rays as applied by Kiatkamjornwong et al. (2002) shows an enhanced maximum

water absorbency of up to 469 g/g. It must be mentioned that for the application of hydrogel in agriculture, a very high WAC is not as important (Zohuriaan-Mehr & Kabiri, 2008) as e.g. for use in diapers or hygiene products. But, our copolymer product exhibits prospects to be developed further. It can be synthesized in one reactor (single step process) and at moderate reaction condition (40 °C and atmospheric pressure).

3.3. Water retention of the products under suction

There are not many data on the capacity of superabsorbent materials to hold absorbed water inside the network when there is a certain outside strain on the material. The most common test method is the absorbency under load (AUL) (Buchholz & Graham, 1998; Zohuriaan-Mehr & Kabiri, 2008). In this test, water absorbency is measured when a certain weight is placed uniformly on the surface of the swollen gel for a period of time. This parameter is appropriate for superabsorbent applications like baby diapers and sanitary napkins.

For other applications, like in agriculture, another parameter is needed to evaluate the physical properties in relation to the mechanical strength. Our set up gave us a new possibility in this respect: to test the water retention capacity when vacuum-like suction is exerted on the material. This was determined by applying a reduced pressure of ca 0.2 bar below the sample, when the swollen hydrogel was spread over a hydrophobic PTFE membrane with pore size 1 μm . The results in Fig. 5 show that the graft copolymer generally has a good stability in water bonding, since it can retain about half of the absorbed water under the strain of this severe suction. The product with 2% crosslinker shows the best performance also under these conditions. It can be concluded that this material has the prospect of being developed further for application in agriculture, to improve the water holding capacity of soils in highly arid regions. This result was obtained without the addition of inorganic fillers to the material or in the production step.

3.4. Kinetic analysis of water transport

To investigate the dynamics of water absorption, the water absorbency of copolymers was observed for a period of time, from zero to maximal absorption capacity. The results were analyzed using Eq. (3), see Section 1.3. The data discussed in Section 3.2 were used for these calculations. The characteristic constants n and k were calculated. The results are presented in Table 1. Especially the value of the diffusional exponent n is interesting since this is the factor that allows us to conclude on the prevailing mechanism of transport. In Section 1.3 it was extensively discussed how we can use the value of $n=0.43$ as a point of distinction. When the value of n is below that, Fickian diffusion will determine the overall rate of absorption. At higher n -values, polymer chain relaxations or network swelling capability will be the governing factor.

The results in Table 1 show a general trend of increasing values of the exponent n at increasing degree of neutralization. It means that at low degree of neutralization Fickian diffusion would be more important while at higher DN chain relaxations is the effect that limits the rate of water penetration. This is in good correspondence to literature data on synthetic water absorbing polymers (Bajpai & Johnson, 2005; Kuipers & Beenackers, 1993; Üzümlü et al., 2006). These authors also show that in most cases of superabsorbent-type materials, relaxation of the macromolecules is the dominant mechanism. However, like in our work it was seen that at low DN Fickian diffusion can be prevailing. At low DN, the number of $-\text{COONa}$ groups attached along the macromolecular chains is much lower than at high DN. This means that there are also fewer Na^+ ions electrostatically bound inside the gel network that can generate an osmotic driving force. In this situation, restrictions from relaxation

movements in the network of the copolymer are less important and logically, Fickian diffusion is the prevailing transport mechanism. At the more important conditions where our gels show the best absorption performance however, the value of n is well above 0.43. This means that for the optimal material, produced at St:AA = 1:2, 2% CL and ca 50% neutralization (see Fig. 4), the rate of water absorption is completely governed by polymer chain relaxations. Thus, the ability of the grafted starch chains to expand allowing the network to swell is the limiting factor, not the osmotic driven diffusion. This knowledge can be very useful in the further development of starch based superabsorbent materials.

4. Conclusions

A superabsorbent product was synthesized by direct grafting of acrylic acid onto cassava starch in the presence of a polymerization crosslinker. The increase of grafting parameters at increased crosslinker concentration indicates that part of the homopolymer formed in the homogenous reaction system becomes incorporated in the grafted network. By variation of the crosslinker content (CL%), an optimum in the water absorbency of up to 114 g $\text{H}_2\text{O}/\text{g}$ could be obtained. Interestingly, this optimum is at 2% CL which does not directly correspond with the best grafting results, obtained at 1.5% CL. A remarkable feature of the product with the best absorption capacity is its ability to retain more than half of this maximum amount of water also under the mechanical strain of severe suction. The good absorption and retention properties obtained in this grafted starch would allow for a further development of the material, e.g. in the agricultural application as a moisture retaining agent in arid soils. The mathematical analysis of the kinetics of water absorption shows that Fickian diffusion is only prevailing at low Na^+ content in the gelled network. At a DN of 50% or more, polymer chain relaxations are the dominant mechanism. At ca 50% neutralization also the best absorption capacity was found so these are the conditions of the highest practical interest.

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